

Aqueous Complexation Reactions Governing the Rate and Extent of Biogeochemical U(VI) Reduction

**Scott C. Brooks^{*1}, Wenming Dong¹, Sue Carroll¹,
James K. Fredrickson², Kenneth M. Kemner³, Shelly Kelly³**
Collaborators: Kent Orlandini³, John Zachara²

¹ *Oak Ridge National Laboratory*

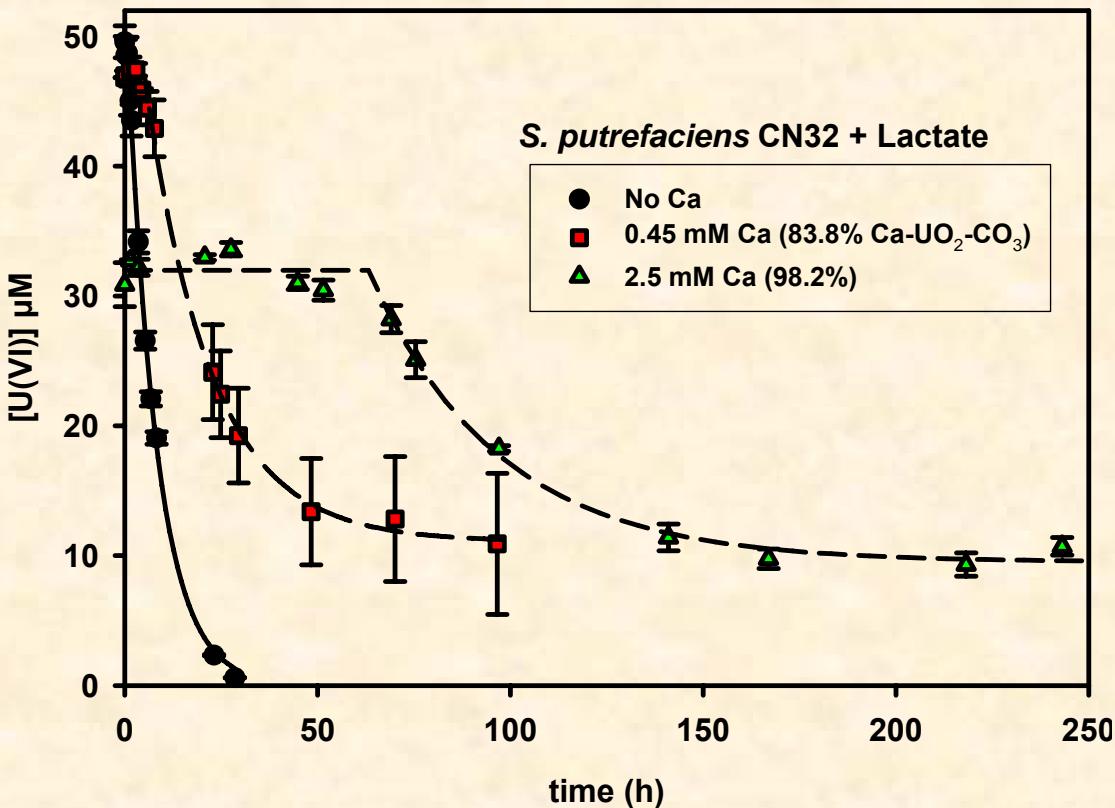
² *Pacific Northwest National Laboratory*

³ *Argonne National Laboratory*



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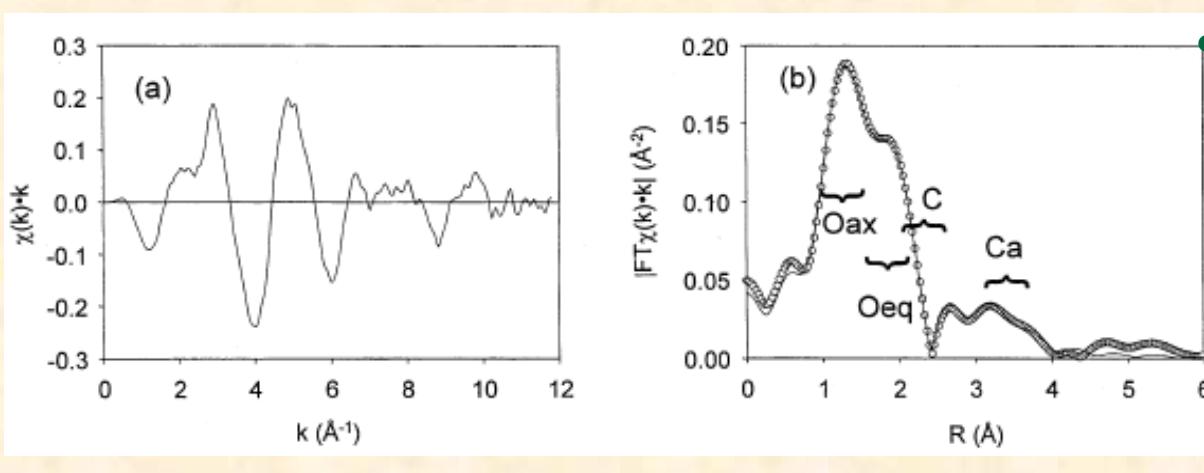
The effect of Ca did not depend on:

- Bacterial strain:
 - S. algae* BrY
 - S. putrefaciens* SN32
 - Desulfovibrio desulfuricans*
 - Geobacter sulfurreducens*
 - G. metallireducens* GS-15
- Antecedent culture conditions: aerobic, anaerobic.
- Electron donor: Lactate, Acetate, H₂.

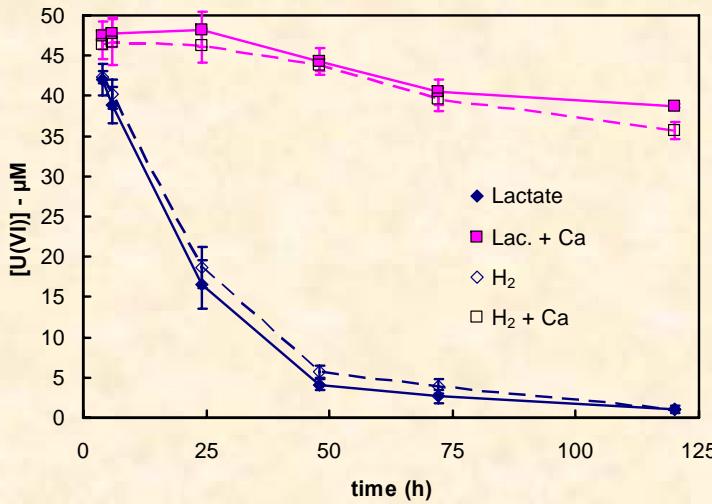
The effect of Ca did depend on:

Electron acceptor:

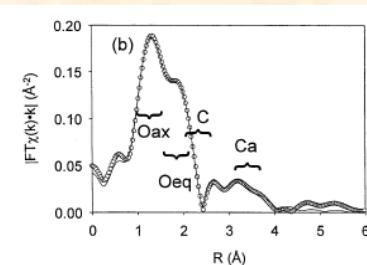
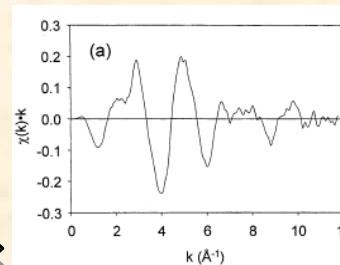
- ✓ U(VI)
- ✗ Tc(VII)
- ✗ Fumarate
- ✗ Co(III)EDTA



(Brooks et al., 2003)



Link between U(VI) speciation and direct bacterial reduction



Implications for Biogeochemical U(VI) Reduction?

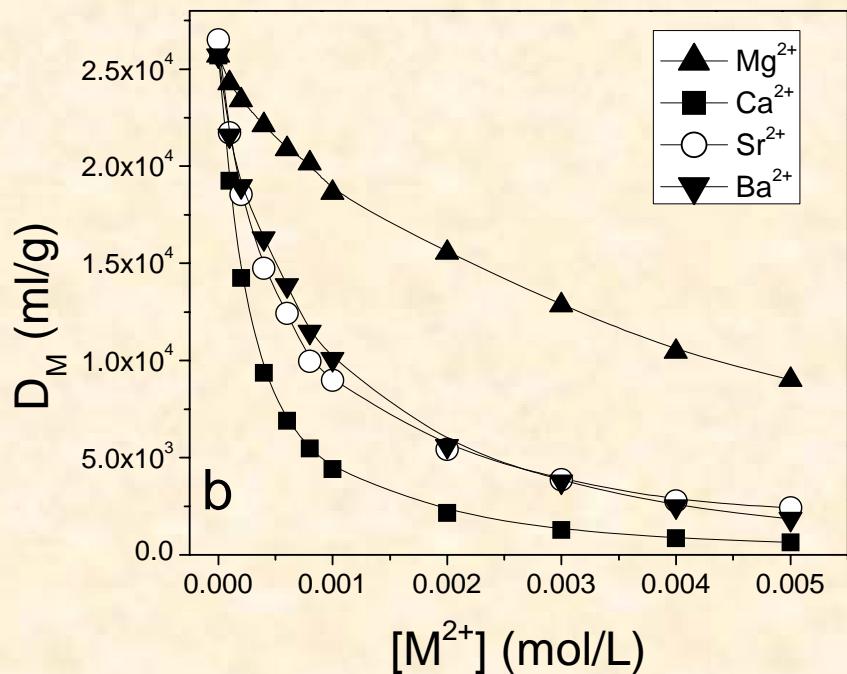
Ternary Complex Formation:

Other M-UO₂-CO₃ complexes exist. Their influence on rate and extent of bacterial U(VI) reduction will be a function of their net charge and stability.

Abiotic Reduction:
Indirect reduction of U(VI) (e.g., surface associated Fe(II)) is inhibited by formation of M-UO₂-CO₃ complexes. Effect proportional to stability constants.

Microbial Reduction:
Retardation of microbial metal reduction activity will be restricted to M-UO₂-CO₃ complexes (i.e., no effect on Fe(III) reduction).

Determination of the formation constants of ternary complexes of uranyl and carbonate with alkaline earth metals (Mg^{2+} , Ca^{2+} , Sr^{2+} , Ba^{2+}) using an anion exchange method (Dong and Brooks, *in review*)



$$\frac{D_0}{D_M} - 1 = K_1 [M^{2+}]_{aq} + K_2 [M^{2+}]^2_{aq}$$

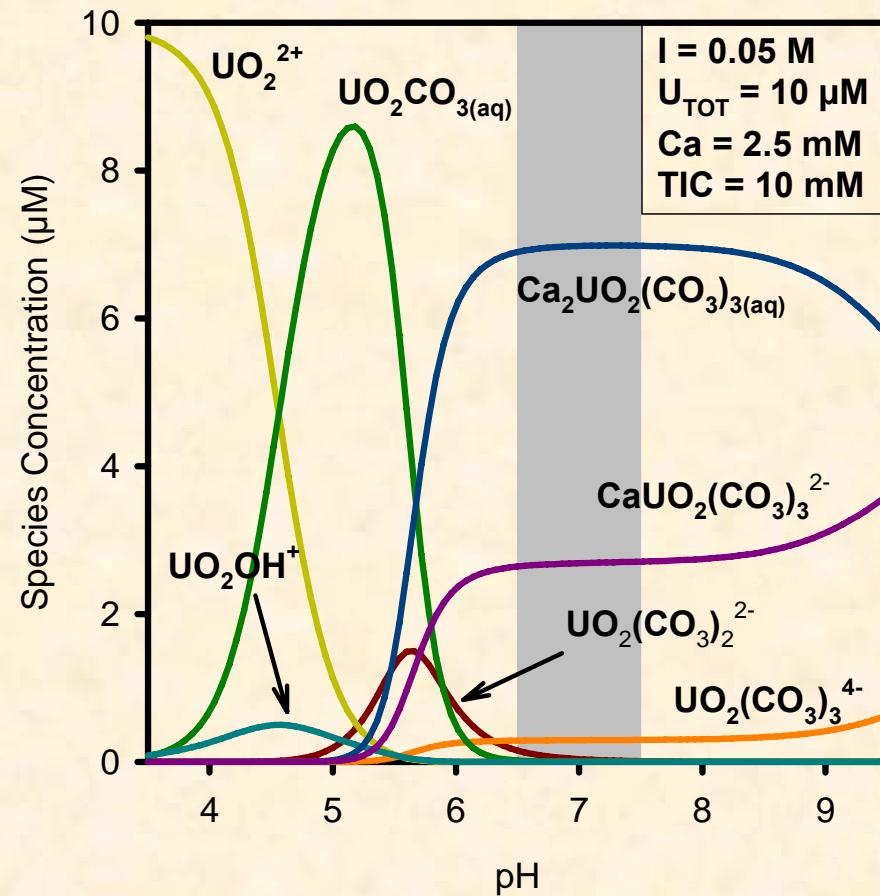
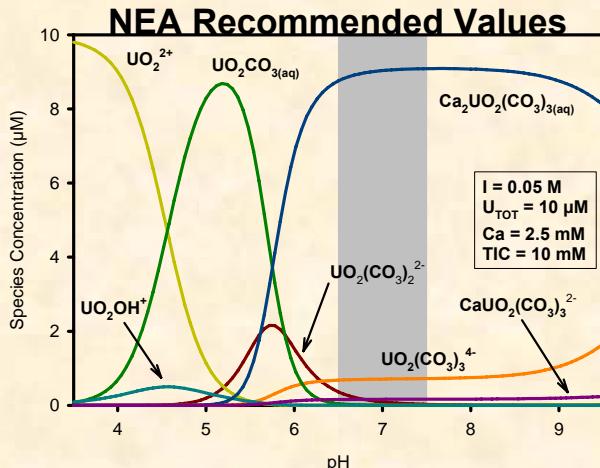
- D_0 , D_M , $[M]$ measured by experiment.
- K_1 and K_2 determined from fit to data.
- F-test to determine the more appropriate model.

Formation constants of the $\text{MUO}_2(\text{CO}_3)_3^{2-}$ (aq) and $\text{M}_2\text{UO}_2(\text{CO}_3)_3^0$ (aq) complexes.

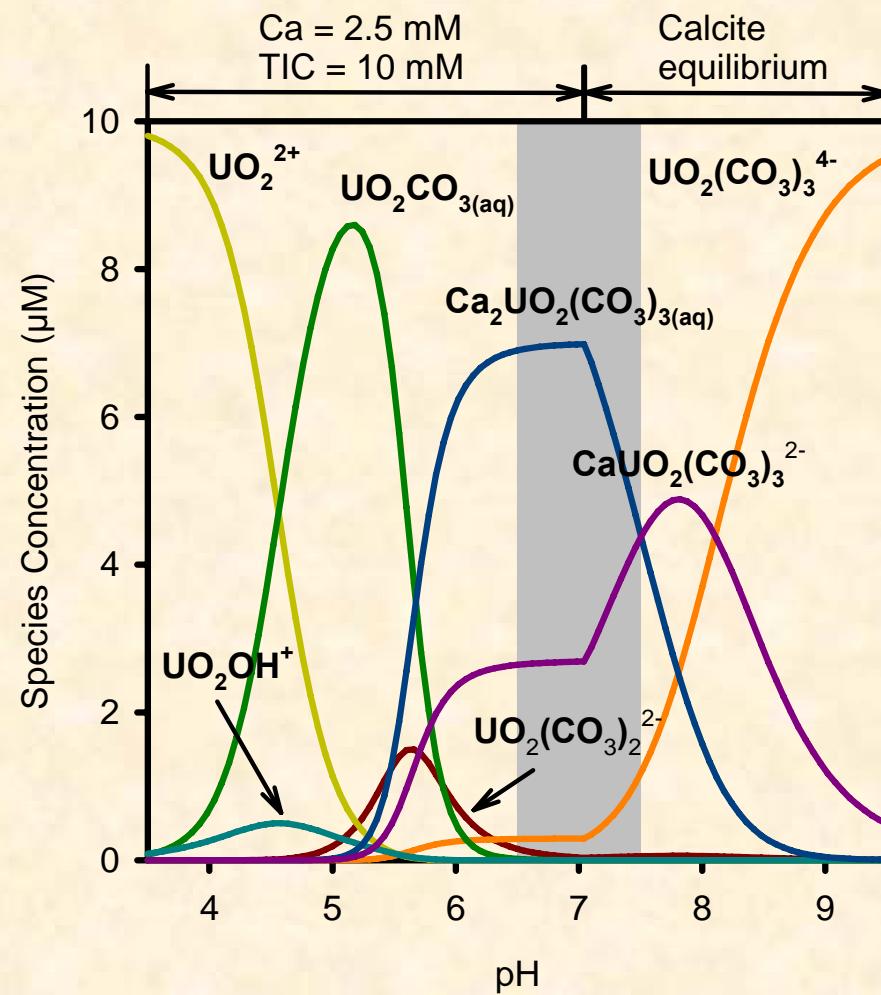
	$\text{MUO}_2(\text{CO}_3)_3^{2-}$	$\text{M}_2\text{UO}_2(\text{CO}_3)_3^0$	
M^{2+}	$\log \beta_{113} (\text{I} = 0)$	$\log \beta_{213} (\text{I} = 0)$	Reference
Mg^{2+}	26.11 ± 0.04	---	This work
Ca^{2+}	27.18 ± 0.06	30.70 ± 0.05	This work
	---	$29.41 \pm 0.7^{\text{b}}$	Bernhard et al., 1996
	$25.6 \pm 0.25^{\text{b}}$	$30.79 \pm 0.25^{\text{b}}$	Bernhard et al., 2001
	---	$29.8 \pm 0.7^{\text{b}}$	Kalmykov and Choppin, 2000
Sr^{2+}	26.86 ± 0.04	---	This work
Ba^{2+}	26.68 ± 0.04	29.75 ± 0.07	This work

^a = marginally significant at $P = 0.0496$ and therefore not accepted .

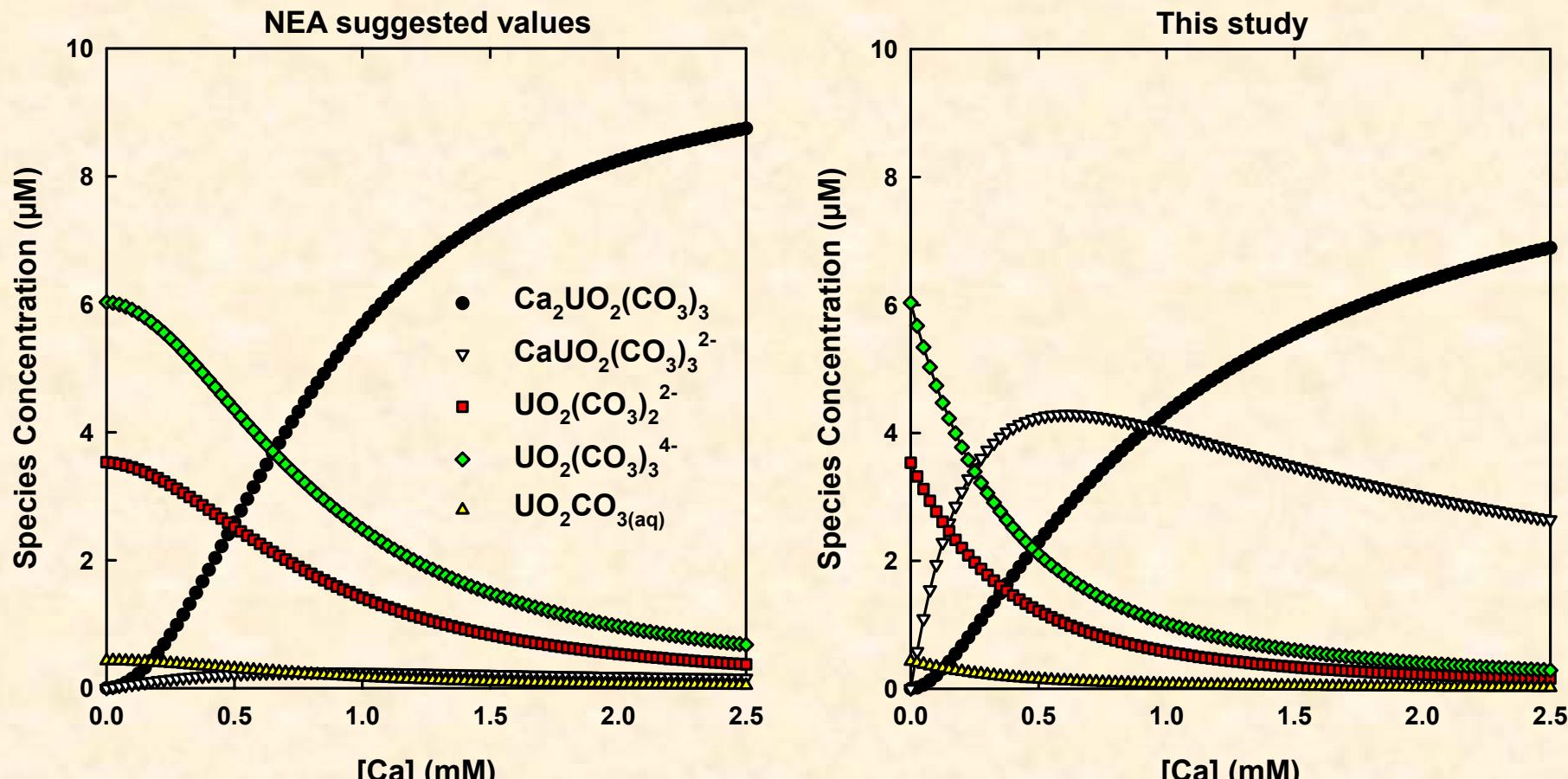
^b = revised to reflect the new recommended value for formation constant of $\text{UO}_2(\text{CO}_3)_3^{4-}$ in Guillaumont et al. (2003).



Implications of our estimated stability constants 1: Speciation as $f(\text{pH})$

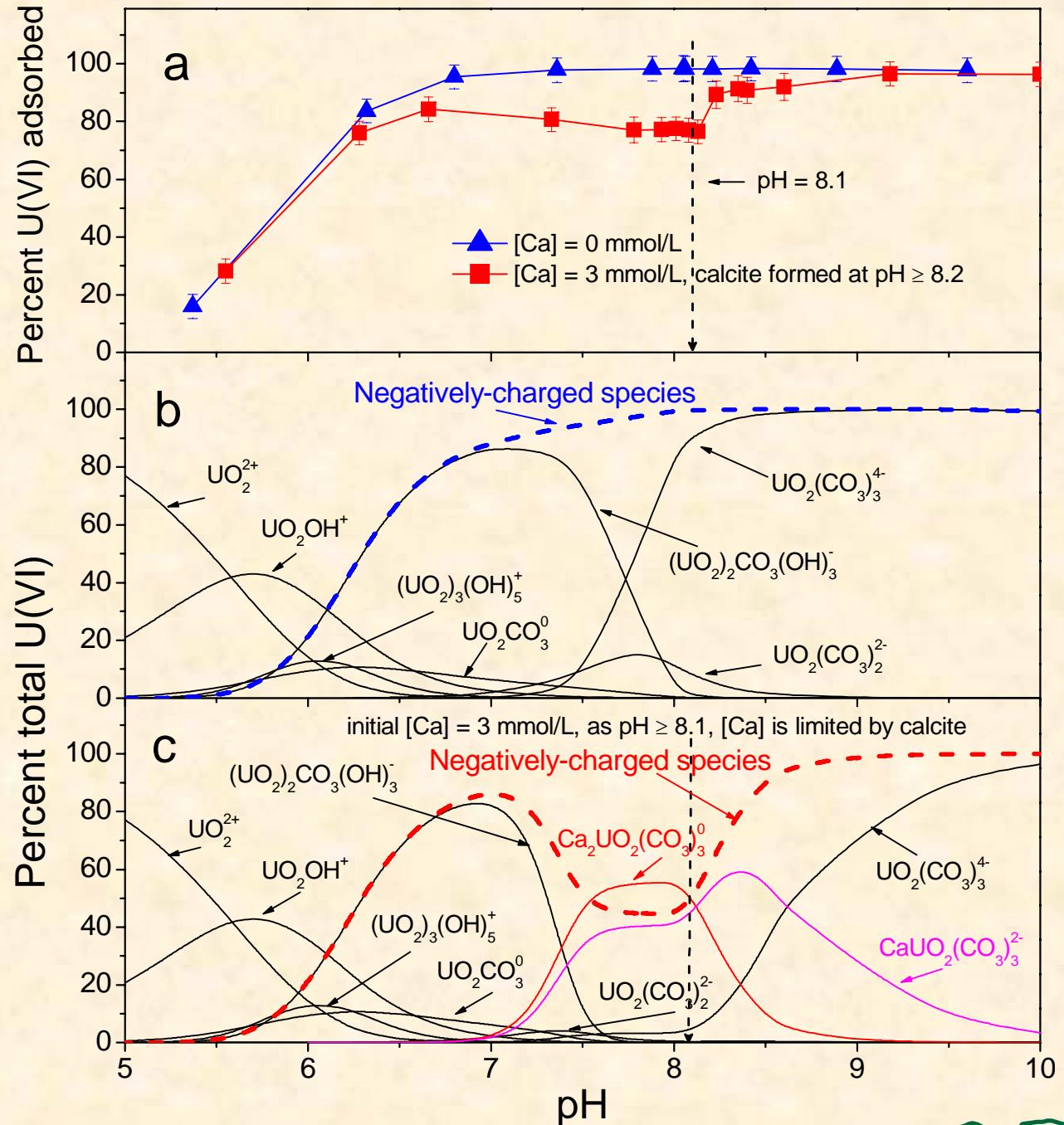


Implications of our estimated stability constants 2: Speciation as $f([Ca])$



$I = 0.05; \text{pH } 8$
 $\text{TIC} = 10 \text{ mM}$
 $\text{U}_{\text{TOT}} = 10 \mu\text{M}$

U(VI) uptake by anion exchange resins inhibited by formation of neutral $\text{Ca}_2\text{UO}_2(\text{CO}_3)_3^0$



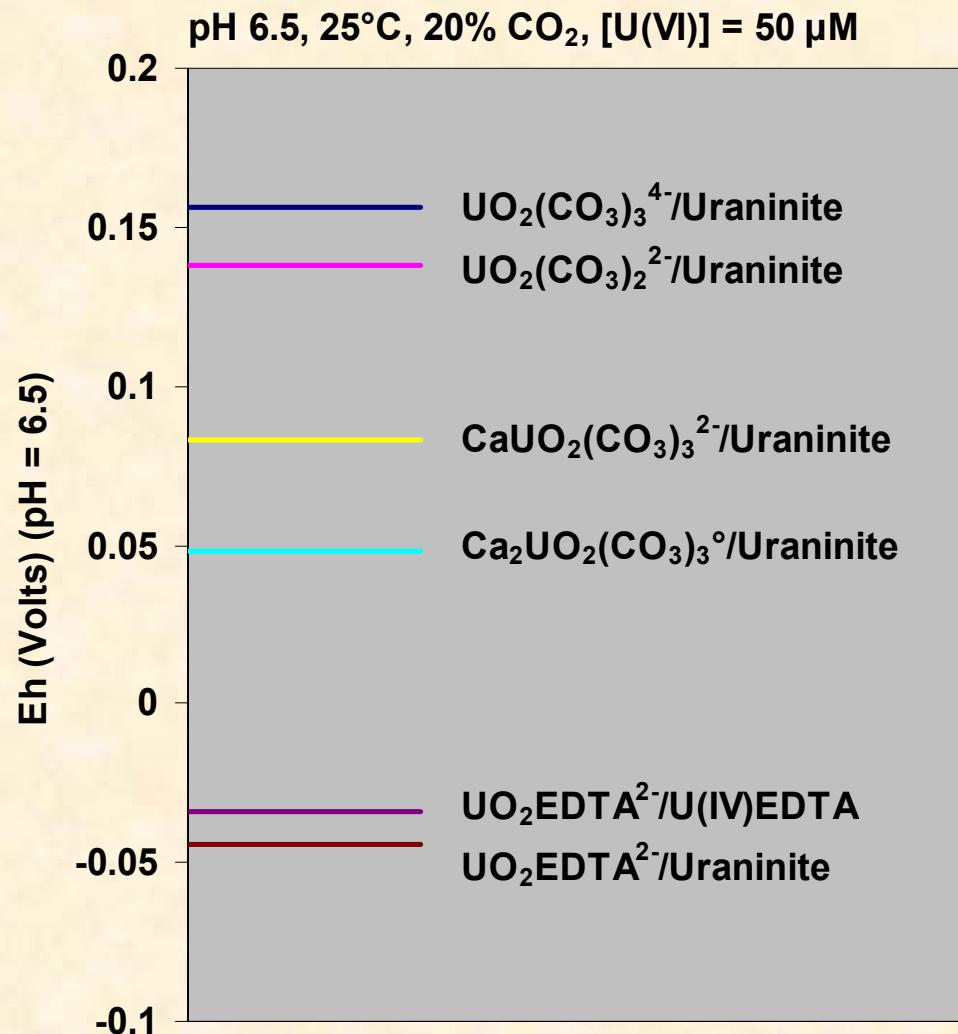
Summary 1:

- Identified and quantified alkaline earth-uranyl-carbonate complexes.
 - Mg & Sr : $\text{MUO}_2(\text{CO}_3)_3^{2-}$ **
 - Ca & Ba : $\text{MUO}_2(\text{CO}_3)_3^{2-}$, $\text{M}_2\text{UO}_2(\text{CO}_3)_3^0$
 - Ca > Ba = Sr > Mg
- $\text{CaUO}_2(\text{CO}_3)_3^{2-}$ complex more important than previously suggested
- Decreased U partitioning to anion exchange resins correlate with predicted species distribution.

Influence of EDTA and pH on Bioreduction of Uranium(VI) in the Presence of Calcium Ions (Dong et al., *in prep*)

U(VI) Speciation : Implications for Bioreduction?

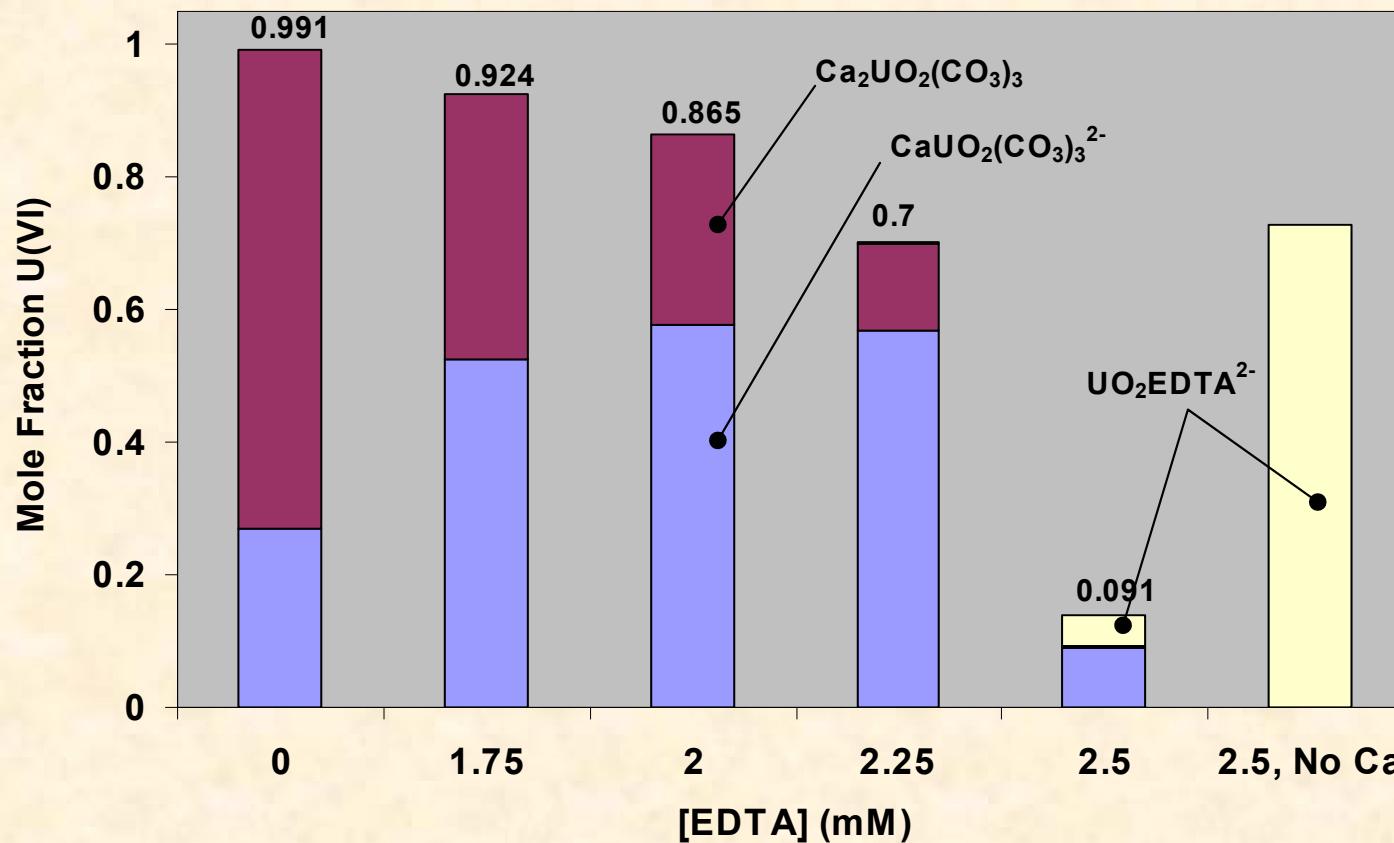
- **Thermodynamic considerations**
 - U(VI) speciation affects reduction potential → energy available to microorganisms.
- **Kinetic considerations**
 - Synthesis of new cell components?
 - Speciation kinetics?



Influence of EDTA and pH on Bioreduction of Uranium(VI) in the Presence of Calcium Ions (Dong et al., *in prep*)

U(VI) Speciation as $f([EDTA])$ at pH 6.5

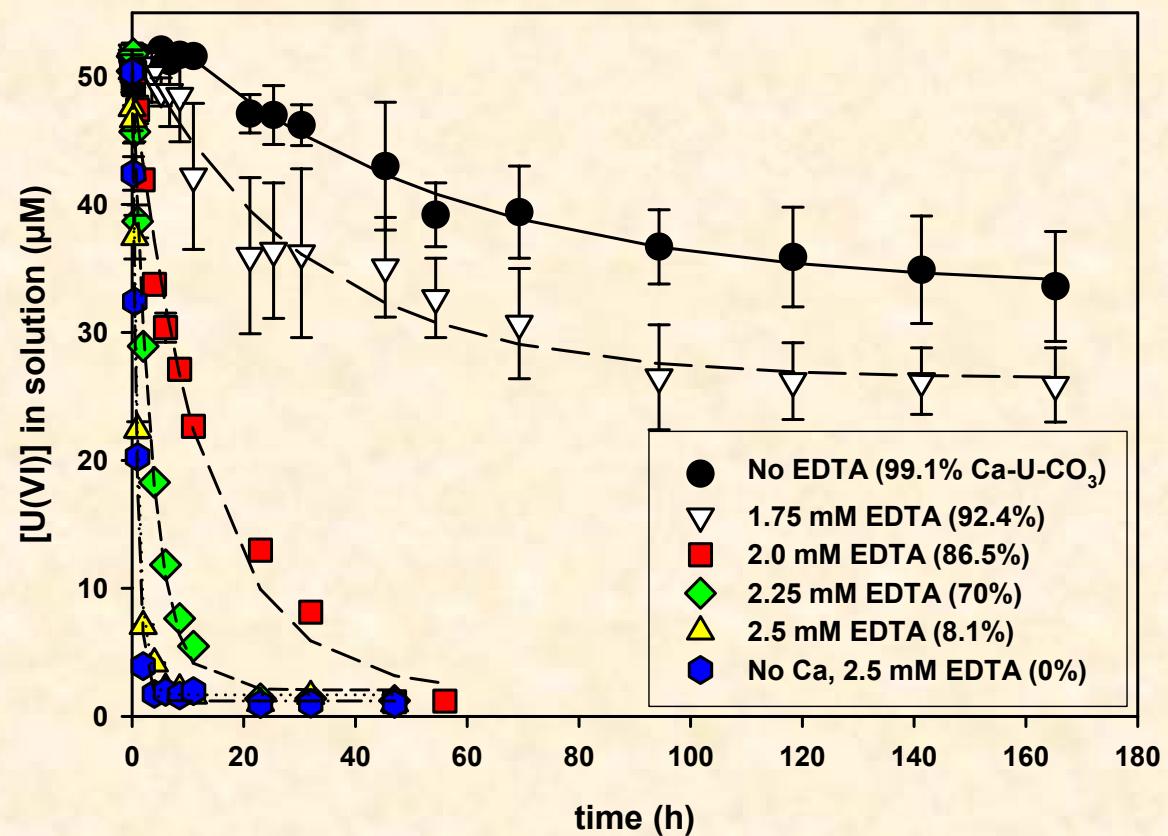
11 mM NaHCO₃, 20% CO₂, pH 6.5, 2.5 mM Ca



UO₂(CO₃)₃⁴⁻ and UO₂(CO₃)₂²⁻ constitute the balance of U(VI) species.

Influence of EDTA and pH on Bioreduction of Uranium(VI) in the Presence of Calcium Ions

- *S. putrefaciens CN32*
 - 11 mM NaHCO₃
 - 20% CO_{2(g)}
 - pH 6.5
 - 2.5 mM CaCl₂
- Increasing [EDTA]:
 - Decreased fraction Ca-U(VI)-CO₃ species.
 - Increased reduction rate.
 - Decreased lag phase.
 - More complete reduction.
 - Lines = pseudo 1° model
- When EDTA present U_{TOT} constant in filtered fraction.

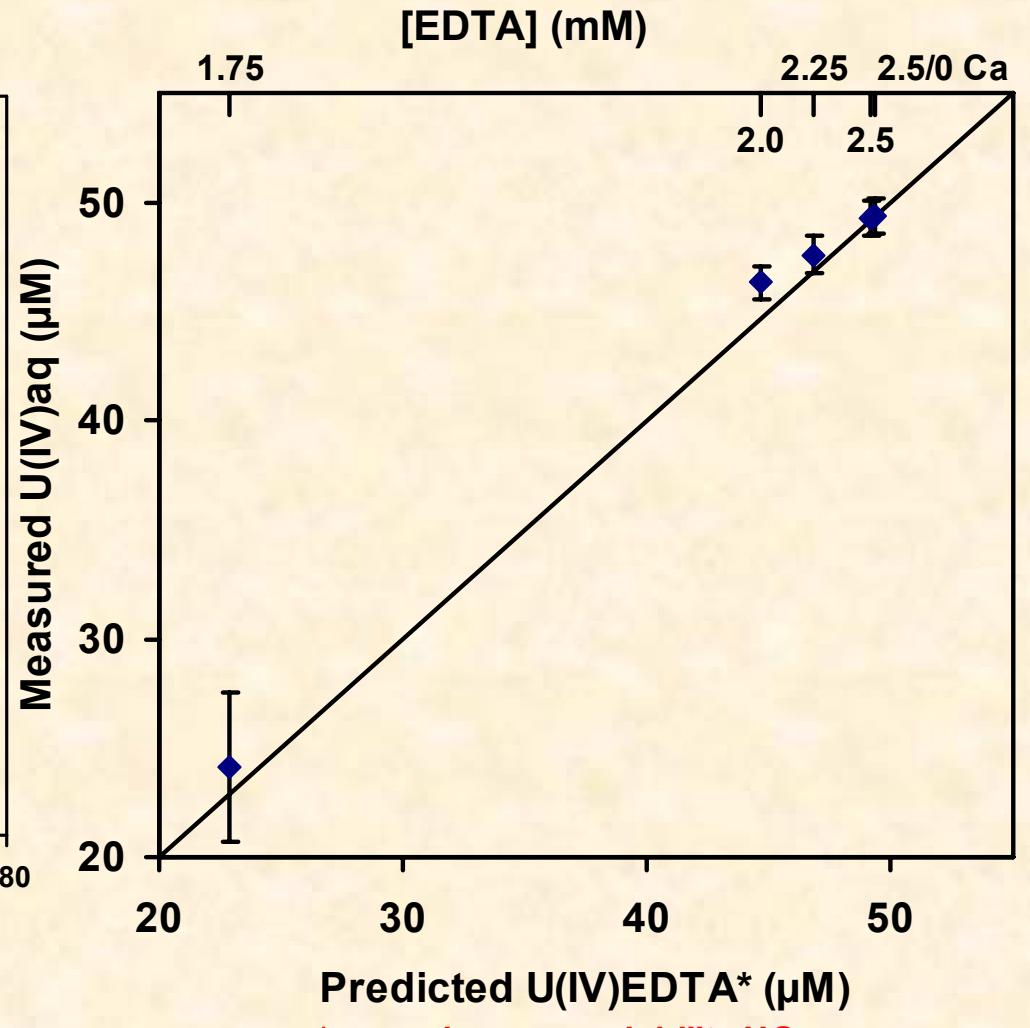
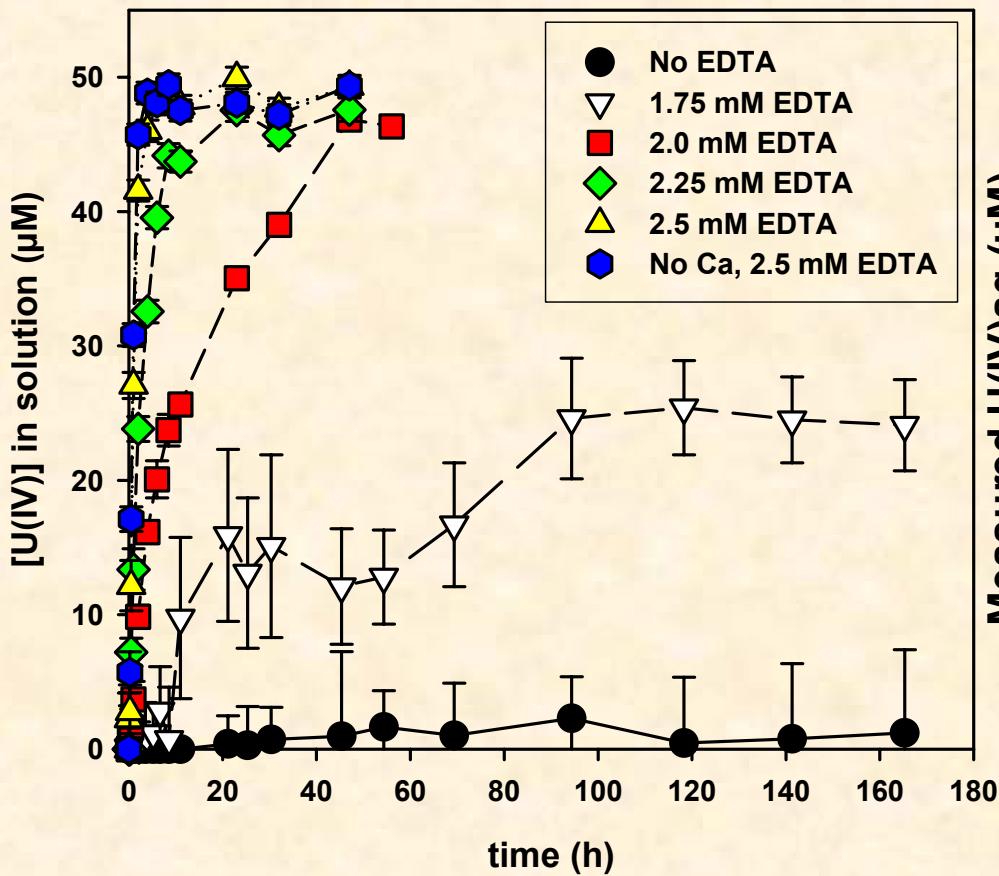


(Dong et al., in prep)

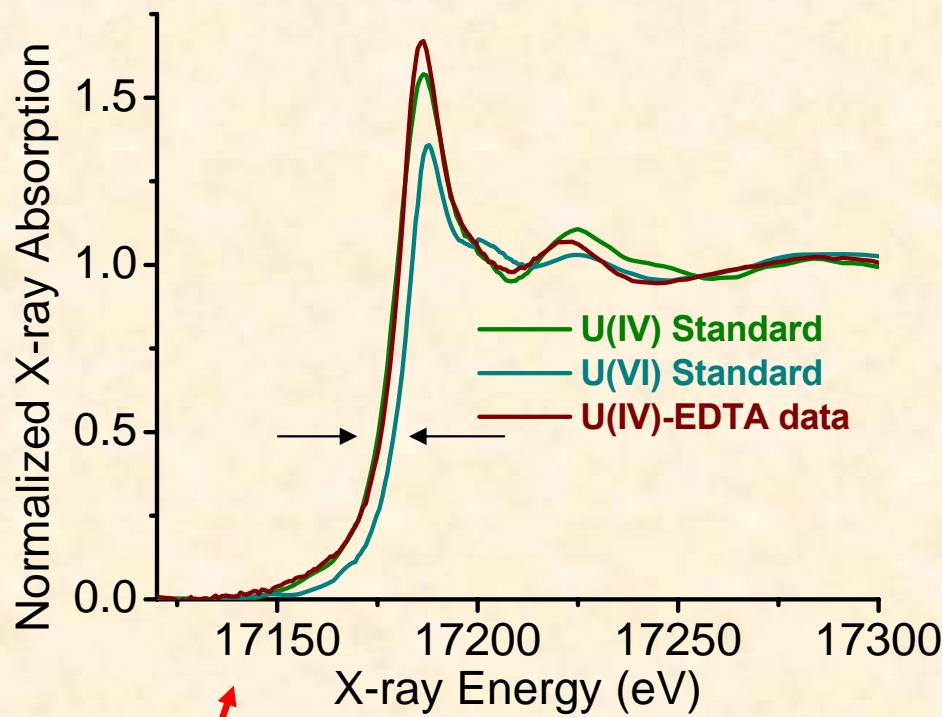
Fate of Biogenic U(IV) in presence of EDTA

(*U(IV) in solution = U(IV) passing 0.2 μm pore size filter)

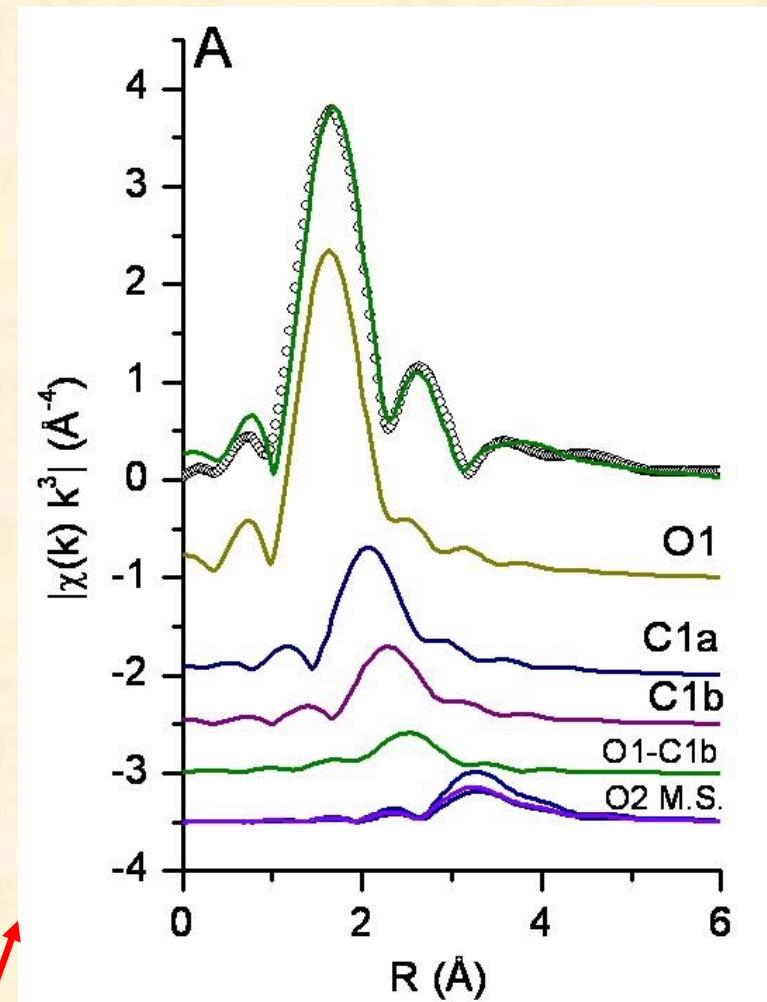
- Suggests that a U(IV) solid phase with a higher solubility than $\text{UO}_{2,\text{am}}$ (Guillaumont et al., 2003) controlled [U(IV)].
- U(IV) stable in solution for at least 5 months (...and counting).



*assuming max solubility $\text{UO}_{2,\text{am}}$

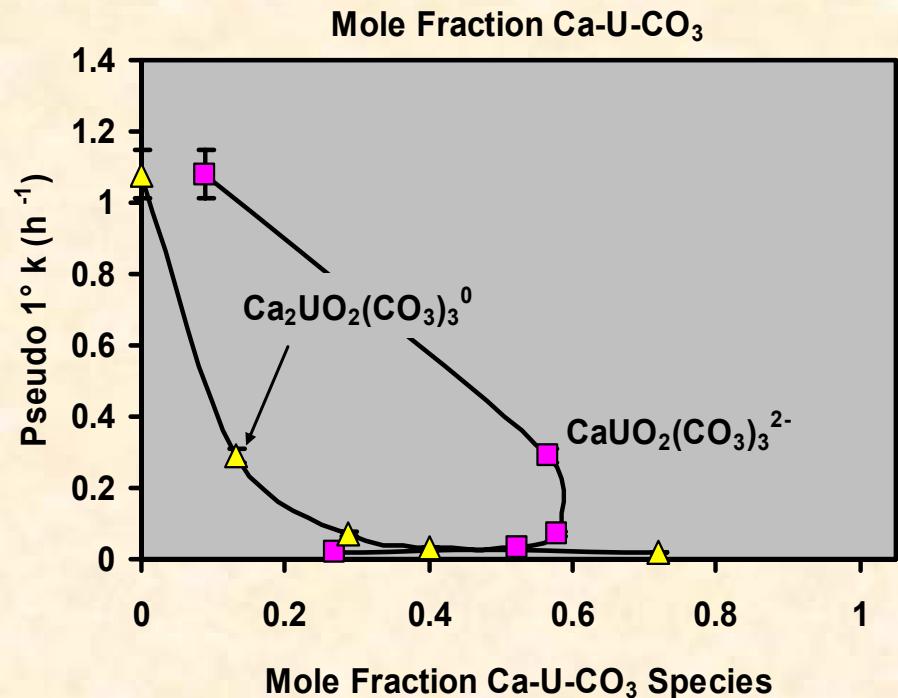
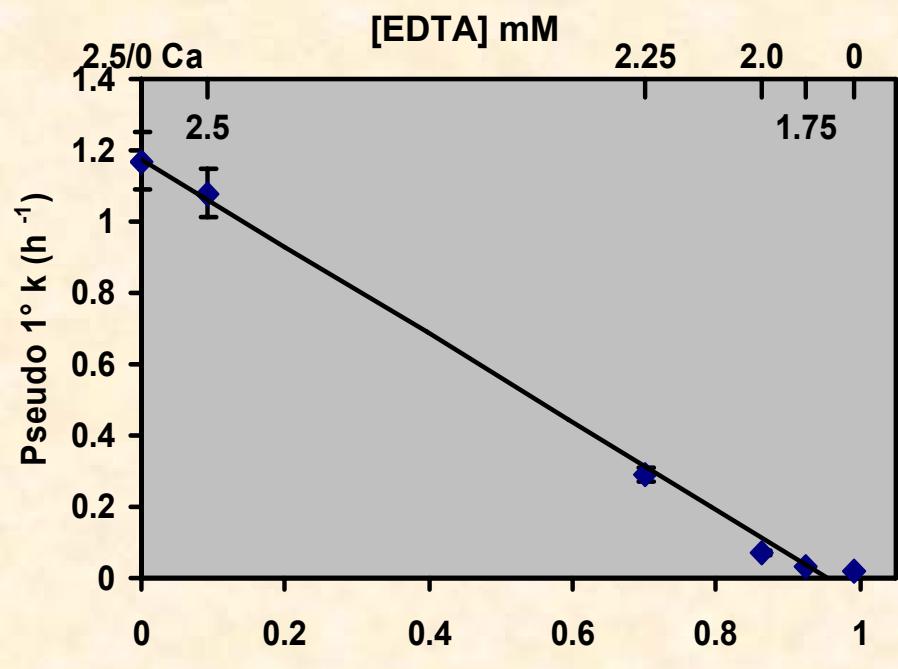
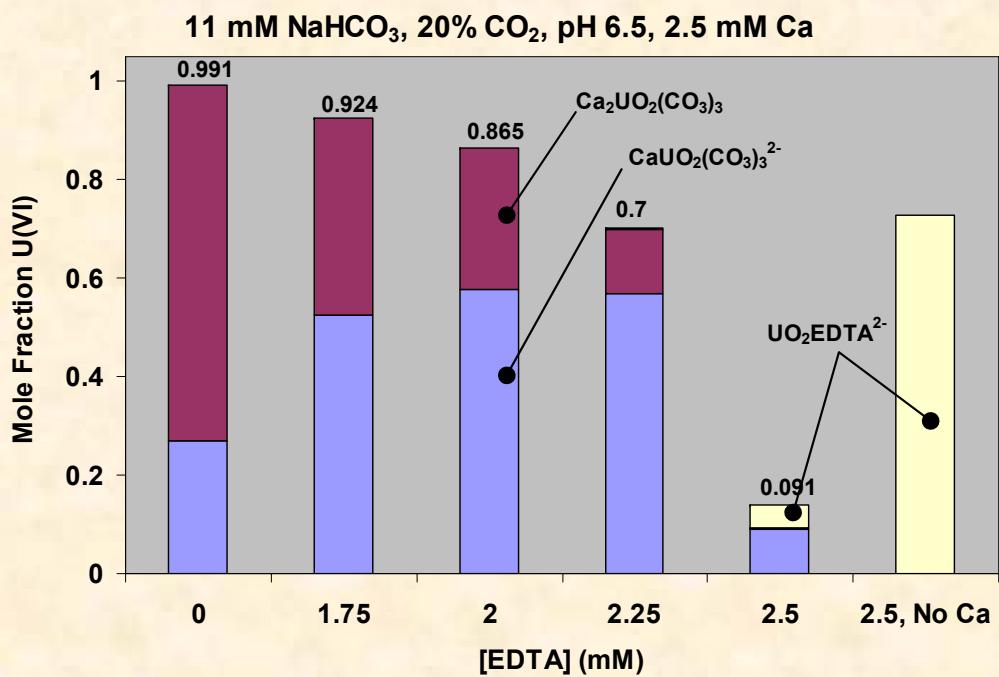


- **U-XANES** verifies that the majority of the U in the sample is in the +4 valence state.

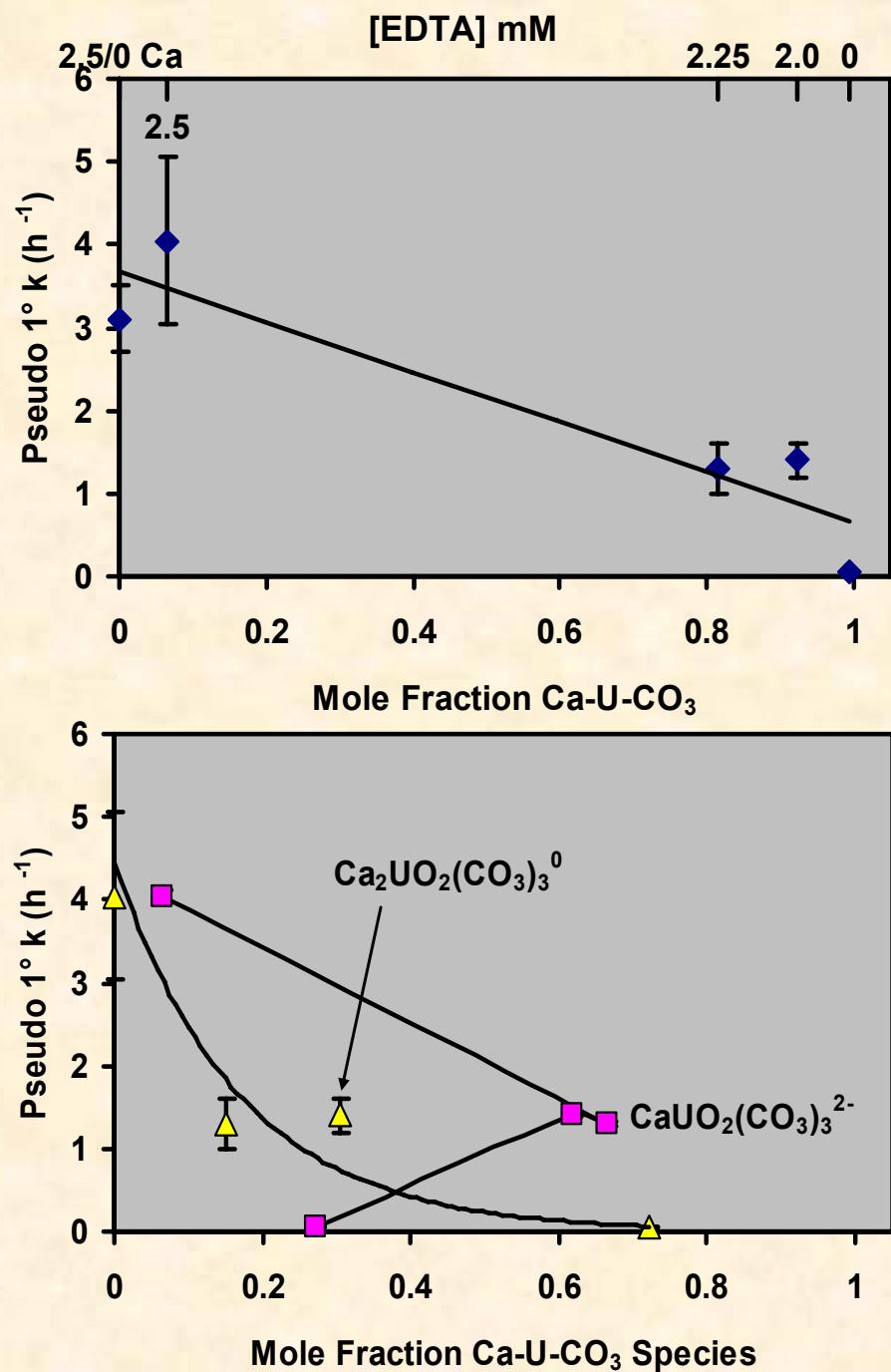
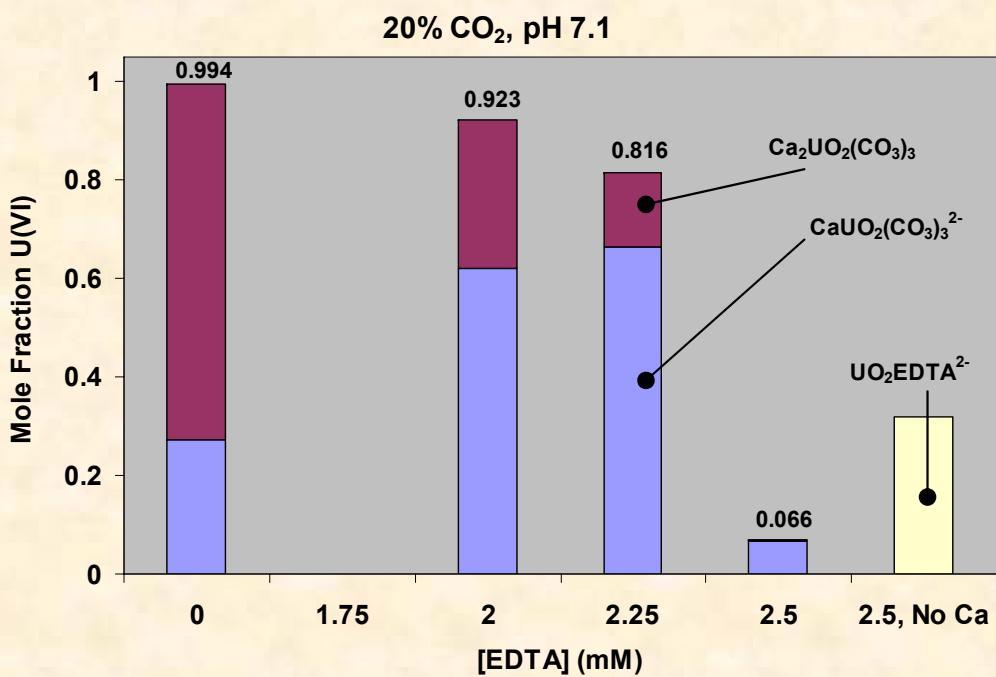


- **U-EXAFS** : No U-U backscatter – indicates dissolved U, not nanoparticles that passed 0.2 μm pores in filter.

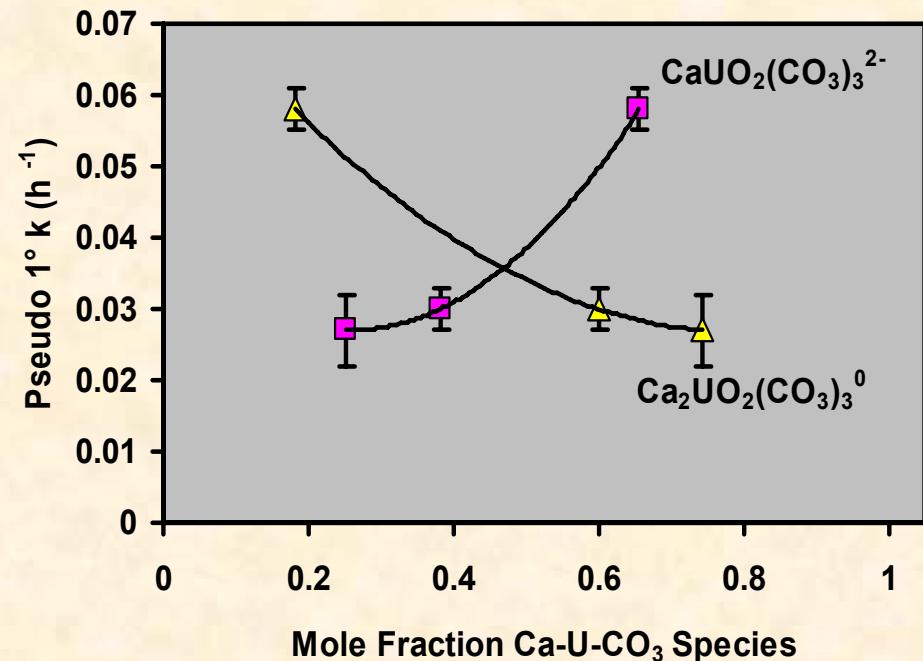
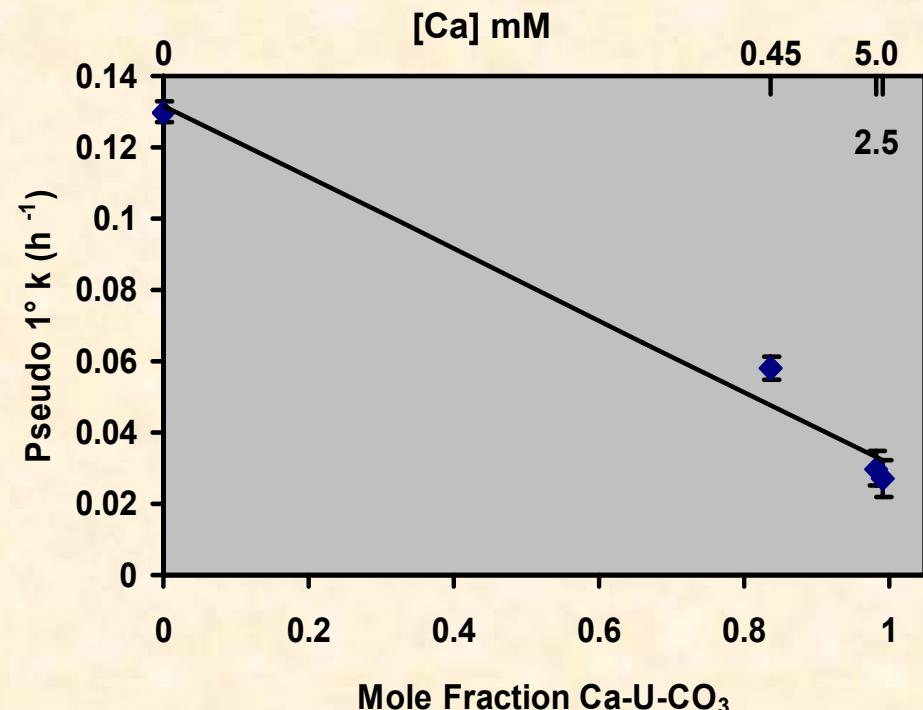
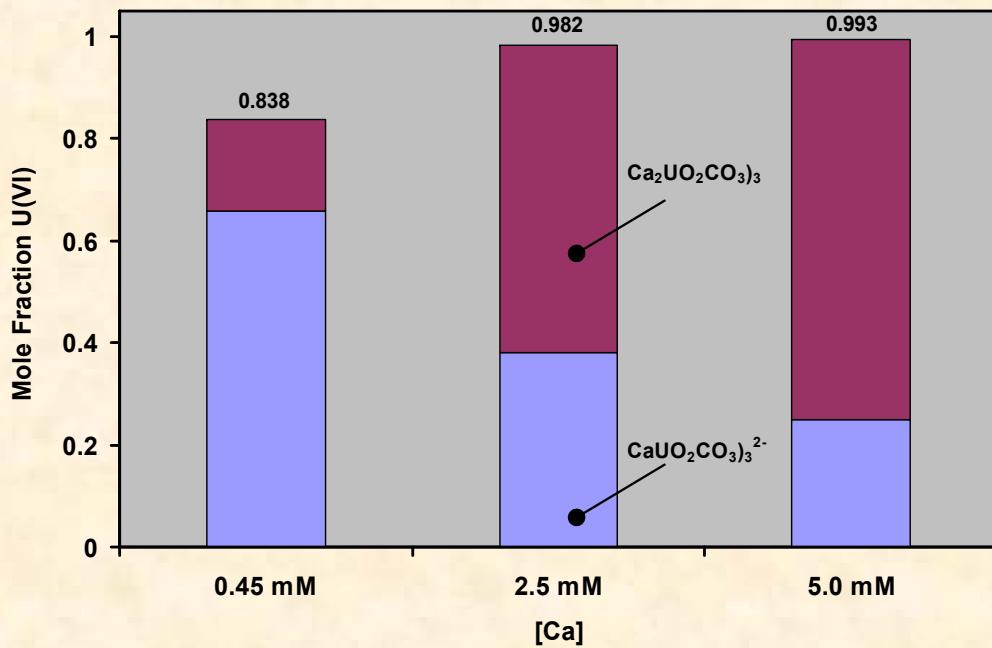
U(VI) speciation controlled by [EDTA] pH 6.5



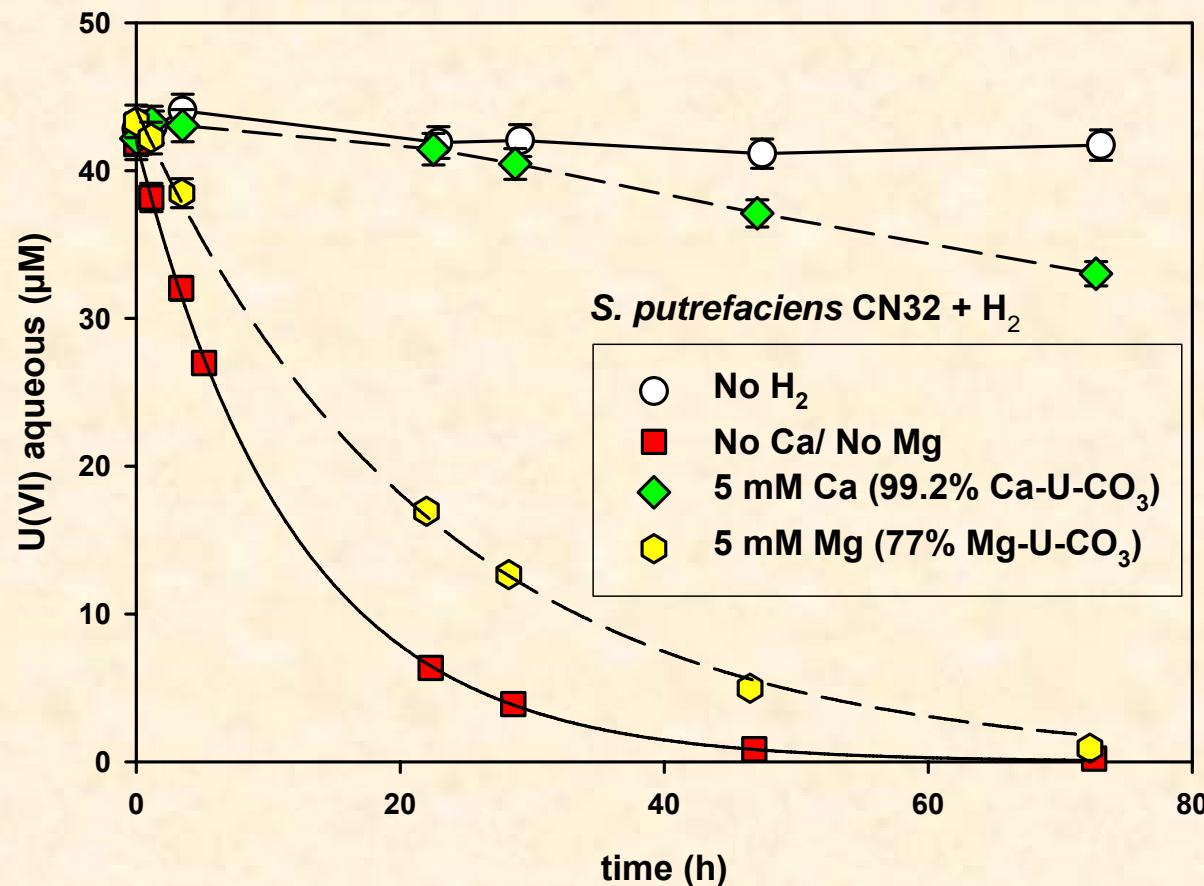
U(VI) speciation controlled by [EDTA] pH 7.1



U(VI) speciation controlled by [Ca] pH 6.9



Effect of Mg on bacterial U(VI) reduction (preliminary):



- Mg slows rate of U(VI) reduction
 - Effect weaker than Ca
 - Mg complex is weaker than the Ca complexes
 - The $\text{MgUO}_2(\text{CO}_3)_3^{2-}$ complex is dominant

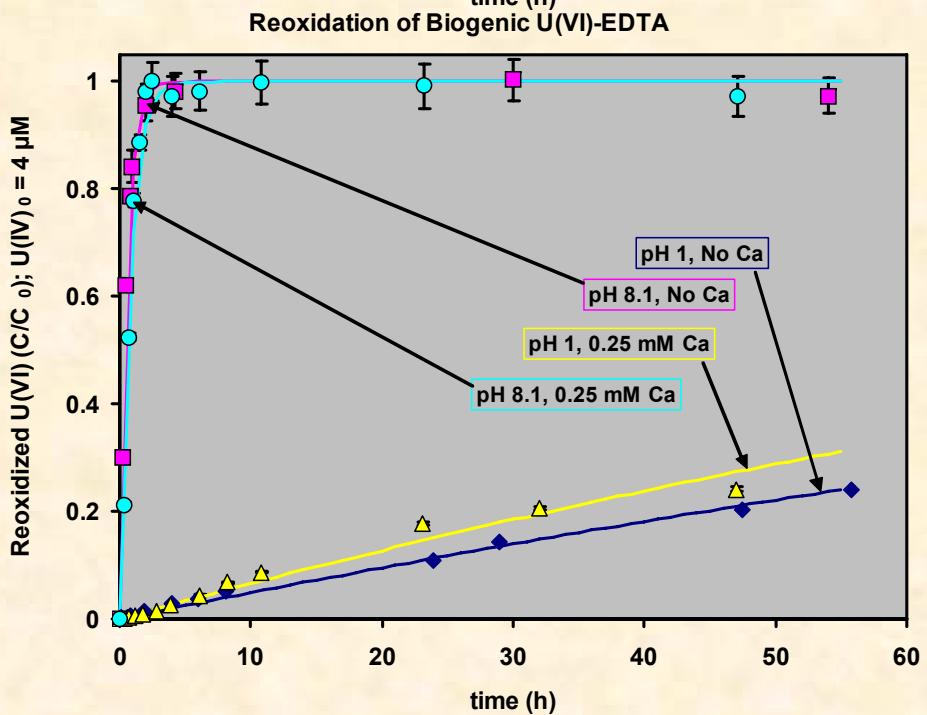
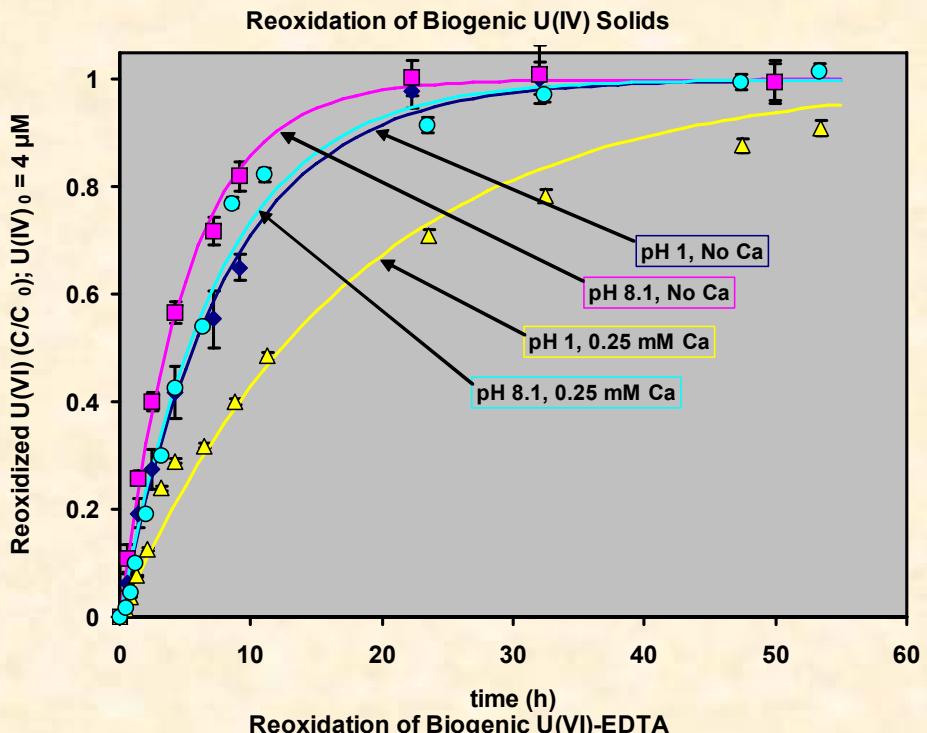
Summary 2:

- **Rate and extent U(VI) bioreduction related predicted speciation.**
 - Tentative evidence that the uncharged $\text{Ca}_2\text{UO}_2(\text{CO}_3)_3^0$ complex governs the observed rate.
- **EDTA additions:**
 - A stable U(IV)EDTA complex generated
 - Suggests that neither $\text{UO}_{2,\text{am}}$ nor Uraninite controlling U(IV) solubility.
- **Nature of thermodynamic and kinetic constraints is not entirely clear:**
 - Thermodynamic constraints do not seem to limit rate or extent U(VI) reduction
 - U(VI)EDTA weaker electron acceptor than the Ca-UO₂-CO₃ species yet is reduced faster and to a greater extent.
 - Analogous species exist for other alkaline earth elements
 - Impact on U(VI) bioreduction related to strength of complex
- **Rate of complex dissociation?**

Reduced Product Stability: Effects of pH, EDTA, and Ca²⁺ on Biogenic U(IV) solids and U(IV)-EDTA Oxidation (Dong and Brooks, *in prep*)

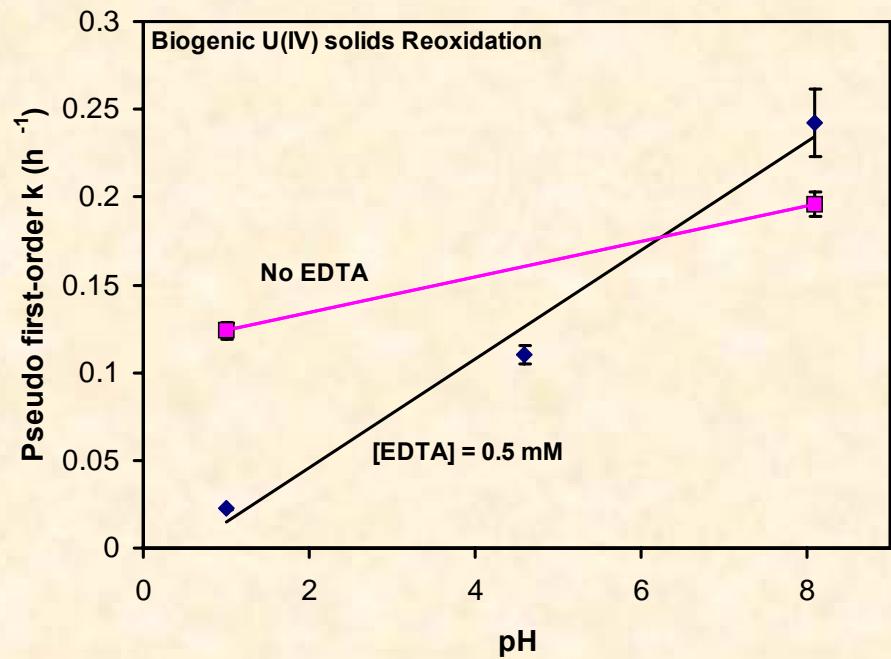
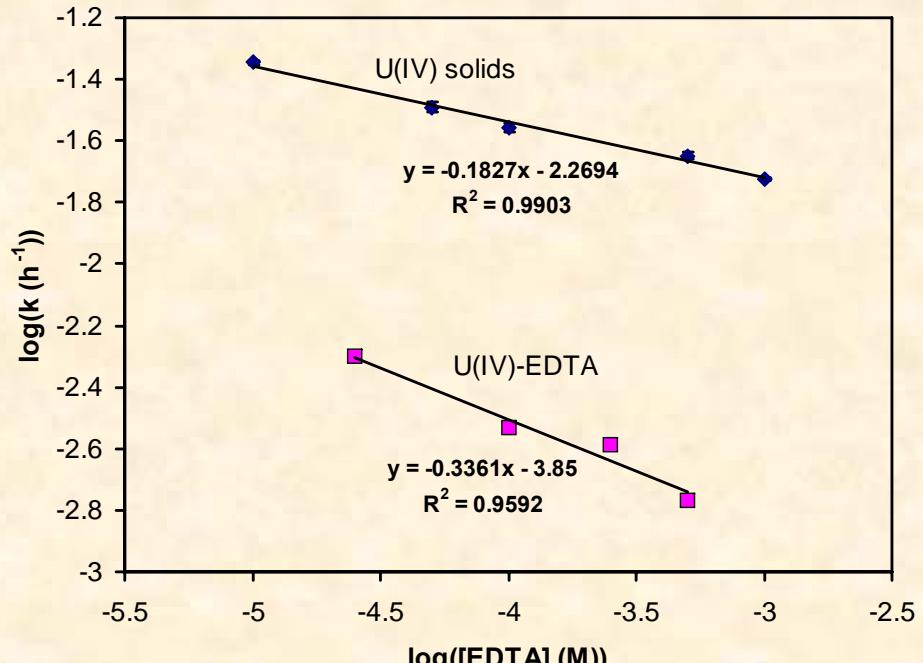
- **Biogenic U(IV) samples prepared anaerobically.**
- **Removed from glovebox and exposed to atmosphere (21% O₂) without stirring/ shaking.**
- **U(VI) monitored over time.**

$$\frac{C(t)}{C(0)} = 1 - \exp(-kt)$$



- The oxidation rate of U(IV) solids and U(IV)-EDTA increased with increasing pH and decreasing [Ca]

- **EDTA slows the rate of biogenic U(IV) oxidation at pH 1.**
- **EDTA enhances the rate of biogenic U(IV) solids oxidation as pH increases.**



Summary 3:

- **Biogenic U(IV) oxidation**
 - Increased with pH
 - Decreased with addition of Ca
- At pH 1 EDTA decreased oxidation rate
- As pH increased, EDTA enhanced U(IV) oxidation rate.
- Improved method to determine U(IV) from difference ($U_{TOT} - U(VI)$) by stabilizing U(IV) in samples.